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Wintering eiders acquire exceptional Se and Cd burdens in the Bering Sea: physiological and oceanographic factors

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ABSTRACT: During late winter (March) in the Bering Sea, levels of Se in livers and Cd in kidneys of spectacled eiders Somateria fischeri were exceptionally high (up to 489 and 312 µg g\(^{-1}\) dry mass, respectively). Comparison of organ and blood samples during late winter, early spring migration, and breeding suggests that the eiders’ high Se and Cd burdens were accumulated at sea, with highest exposure during winter. High exposure may have resulted from high metabolic demands and food intake, as well as concentrations in food. In the eiders’ remote wintering area, their bivalve prey contained comparable Se levels and much higher Cd levels than in industrialized areas. Patterns of chlorophyll \(a\) in water and sediments indicated that phytoplankton detritus settling over a large area was advected into a persistent regional eddy, where benthic prey densities were higher than elsewhere and most eider foraging occurred. Se and Cd assimilated or adsorbed by bloom materials apparently also accumulated in the eddy, and were incorporated into the bivalve prey of eiders. Atmospheric deposition of dust-borne trace elements from Asia, which peaks during the ice-edge phytoplankton bloom from March to May, may augment processes that concentrate Se and Cd in eider prey. Compared with freshwater birds, some sea ducks (Mergini) accumulate much higher concentrations of trace elements, even with the same levels in food, with no apparent ill effects. Nevertheless, the absolute and relative burdens of different elements in sea ducks vary greatly among areas. Our results suggest these patterns can result from (1) exceptional accumulation and tolerance of trace elements when exposure is elevated by high food intake or levels in food, and (2) atmospheric and oceanographic processes that concentrate trace elements in local benthic food webs.

KEY WORDS: Spectacled eider · Sea ducks · Body condition · Selenium · Cadmium · Trace elements in food webs · Trace metals · Bedload transport · Aerial deposition · Atmospheric transport

INTRODUCTION

Sea ducks (tribe Mergini) that forage for much of the year in marine waters often have high trace element burdens that would cause serious reproductive problems in freshwater birds (Ohlendorf et al. 1986, Henny et al. 1995, Heinz 1996, Trust et al. 2000). However, the particular trace elements that are elevated in sea ducks can vary substantially among species and areas (Stout et al. 2002, Savinov et al. 2003, Mal- lory et al. 2004). For example, in benthic-feeding sea ducks of remote Arctic regions, Se and Cd may both...
reach high levels (Trust et al. 2000), or Cd may be very high while Se is relatively low (Wayland et al. 2001b). Compared with these sea ducks, marine birds that feed in the water column often have similarly high concentrations of Cd and much higher levels of Hg, but generally only low levels of Se and Cu (Norheim 1987, Honda et al. 1990, Savinov et al. 2003). Thus, although high trace elements in these birds do appear related to living in a marine environment, the importance of factors causing element accumulation in prey seems to differ between benthic and epipelagic food webs. For benthivores, these factors also result in quite different geographic patterns of exposure to different trace elements.

High levels of Se in marine birds have been of particular interest. Although Se has a variety of physiological functions, it is often asserted that marine mammals accumulate Se in their livers to detoxify high levels of Hg (Ikemoto et al. 2004). Piscivorous and planktivorous birds often show positive correlations between total Hg and Se in the liver (Norheim 1987, Kim et al. 1996b). Studies of captive quail *Coturnix coturnix* and adult mallards *Anas platyrhynchos* indicate that Se accumulates in liver in response to Hg exposure and probably protects against Hg effects (El-Begearmi et al. 1977, Heinz & Hoffman 1998). However, marine birds often have much higher levels of Se relative to Hg than the 1:1 molar ratio thought appropriate for Hg detoxification, and the magnitude (and sometimes direction) of correlation between Se and Hg are highly variable (Goede & Wolterbeek 1994, Trust et al. 2000, Wayland et al. 2001b, Ikemoto et al. 2004).

High burdens of trace elements in sea ducks raise questions about toxicity. For example, sea ducks often have liver Se levels far higher than those that can impair reproduction and survival in freshwater birds (Henny et al. 1995, Heinz 1996, Stout et al. 2001). With no overt ill effects, common eiders *Somateria mollissima* accumulated much higher levels of Se than did mallards fed food containing the same Se concentrations (Franson et al. 2007). Nevertheless, liver Se concentrations in the eiders increased greatly with increasing concentrations in food. Thus, despite physiological differences that lead to greater accumulation and tolerance of trace elements by sea ducks, their tissue concentrations still depend strongly on levels of exposure. Regardless of toxicity, it remains unclear why trace element concentrations in sea ducks vary so widely among areas that are far from direct contaminant sources.

Atmospheric transport and deposition of trace elements attached to dust particles can be an important source of anthropogenic elements in regions far from their initial source (Yu et al. 2008). For example, recurrent episodes of element-laden ‘Arctic haze’ in northern Alaska, and deposition of trace elements in surface waters of the North Pacific Ocean, have been traced to atmospheric transport from Asia (Rahn et al. 1981, Ranville et al. 2010). In waters with substantial atmospheric deposition (including wet deposition), anthropogenic aerosols can be the source of most trace elements associated with sinking particles (AMAP 1998, Ho et al. 2010).

High demand for trace elements in the upper water column of the ocean, especially during intense phytoplankton blooms, has resulted in algal adaptations for efficient uptake of essential elements (Fisher & Reinfeelder 1995, Zhang 2000). In addition to direct assimilation, even larger amounts of some trace elements (including a portion of Se) can be adsorbed extracellularly or bound via ligands to phytoplankton cells, algal and zooplankton detritus, flocculated exudates, and fecal pellets (Cohen et al. 1992, Ho et al. 2010, Strmecki et al. 2010). Once bloom-derived materials sink to the bottom, bedload transport can redistribute deposited organic matter and associated trace elements (Yao & Zhang 2005). These processes could lead to spatial variations in uptake of elements by benthic food webs (Thorsson et al. 2008).

These various processes of trace element transport and movement through marine systems have been well documented independently. However, they have not been integrated to link patterns of atmospheric deposition, assimilation or adsorption to bloom materials, redistribution of settled organic detritus, and spatial variation of elements in benthic animals. With rapid anthropogenic change, such linkages may become increasingly important for entire food webs, and especially for top predators (Stewart et al. 2010, Komoroske et al. 2012).

An example of such a top predator is the spectacled eider *Somateria fischeri*. Of their world population of about 370 000, ~5% breed on the Yukon-Kuskokwim (Y-K) Delta of Alaska, ~5% on the North Slope (Arctic coast) of Alaska, and ~90% on the Arctic coast of Russia (Fig. 1) (Petersen et al. 2000). These eiders are present in their breeding areas from about late May through August, and in their wintering region from November through mid-April. This species’ wintering area was first documented in 1995; in that year and 8 subsequent years in which they have been located (1996–1999, 2001, 2008–2010), the eiders have been found during March–April in a region of about 100 × 150 km that is 60 to 80 km southwest of St. Lawrence Island in the Bering Sea.
Lovvorn et al.: Trace elements in eiders

(Fig. 2) (Larned et al. 2012). In that area, the entire population occurs in leads (open-water areas) scattered through pack ice, in water 40 to 70 m deep. Spectacled eiders collected there in late March 2001 had been eating almost exclusively the abundant deposit-feeding bivalve *Nuculana radiata* (Lovvorn et al. 2003). In the present study, we measured trace elements in spectacled eiders in their wintering area. We compared those element concentrations with published data for this species during early spring migration, soon after migrations of differing routes and durations, and through the breeding period. We found levels of Se and Cd in wintering spectacled eiders to be remarkably high, and that these elements appeared to be accumulated while the eiders were in their wintering area. In that area, we examined spatial patterns of chlorophyll in the water column and sediments, and of trace elements in sediments and benthic prey. These data suggest that oceanographic concentrating mechanisms, and perhaps atmospheric deposition of trace elements, are key facilitators of high physiological uptake by these eiders.

**MATERIALS AND METHODS**

Trace elements in spectacled eiders, bivalve prey, and other sea ducks

Wintering spectacled eiders were located from helicopters deployed from an icebreaker, and were collected over decoys with shotguns and steel shot (Lovvorn et al. 2003). On 19 March 2001 we collected 39 eiders in this manner at 1 site (62° 40.9’ N, 173° 22.7’ W), and near this site on 22 March 2001 we salvaged 1 adult male and 2 adult females after they collided with the ship at night. One adult male was shot near a lead without decoys on 19 April 1999, and was included with the March 2001 sample. Eiders were frozen until analyzed.

In the laboratory, samples (2 to 5 g fresh mass) of liver, kidney, and pectoral muscle were removed from thawed birds and analyzed for 17 trace ele-
ments with an Elan 6100 inductively coupled plasma (ICP) mass spectrometer (PE Sciex) at the Wyoming State Veterinary Laboratory. Detailed laboratory procedures are described in the Supplement (www.intres.com/articles/suppl/m489p245_supp.pdf).

After removing gut contents and tissue samples for elemental analyses, the eiders were measured and then ground for determination of total body water (oven drying), lipid (Soxhlet extraction), and ash (incineration in a muffle furnace). Total body protein was calculated as the difference between lipid-free dry mass and ash, and body protein was corrected for structural body size (Lovvorn et al. 2003).

For approximate comparison with liver Se levels of eiders collected on and near wintering areas, we estimated liver concentrations from Se measured in the blood of eiders captured on breeding areas on the Y-K Delta (Grand et al. 2002) and the North Slope of Alaska (Wilson et al. 2004) (Fig. 1). An equation relating Se levels in blood (SeB; µg g⁻¹) to levels in liver (SeL; µg g⁻¹ dry mass) for common eiders during the breeding season in Arctic Canada (Fig. 1 in Wayland et al. 2001a), ln SeB = −0.67 + 0.69 ln SeL (r² = 0.28, p < 0.01), was rearranged to yield:

\[ Se_L = \left( \frac{Se_B}{0.5117} \right)^{1.449} \quad (1) \]

Given the relatively low coefficient of determination (r²) and possible seasonal and annual variations, resulting predicted values of liver Se should not be interpreted quantitatively, but only as indicating qualitative trends (Wayland et al. 2001a). Nevertheless, on the North Slope, liver Se levels predicted from blood samples of 14 prebreeding adult males in 1996 (Wilson et al. 2004) did not differ from actual liver Se concentrations in 4 prebreeding adult males salvaged from different years, element levels in eiders soon after arrival at nesting sites reflect exposure during winter and migration in offshore marine areas, where trace elements in benthic prey are not expected to exhibit synchronous between-year variations in the same direction over such large regions. (Note that the small breeding population on the North Slope, about 5% of the total population, is closely protected and sampling of liver and blood from the same individuals is not possible.)

From 9 May to 2 June 2006, and 18 May to 12 June 2007, the eiders’ main bivalve prey when they were collected, Nuculana radiata (Lovvorn et al. 2003), was sampled by an otter trawl with a 7 m footrope (2006) or by a 4-m beam trawl (2007) at stations throughout the study area south of St. Lawrence Island (Fig. 2). Cruises in May 2006 and 2007 were our first opportunity to take an icebreaker back into this area after collecting spectacled eiders in March 2001, which revealed their very high contaminant levels. Specimens of N. radiata were frozen immediately after collection. After later thawing in the laboratory, soft tissues of N. radiata were physically separated from the shell, and combined for trace element analysis by methods described above for bird tissues.

Tissue concentrations of selected trace elements in sea duck species that winter in marine environments were compiled from the literature. In cases where concentrations were expressed only in terms of fresh mass, we converted values to dry mass assuming dry mass percentages of 30% for liver and 23% for kidney (see the Supplement).

Chlorophyll a in the water column and sediments

During 19 May to 15 June 2007 throughout the study area, water samples (250 ml) from up to 12 depths at each station were filtered through Whatman GF/F filters and extracted in 90% acetone for 24 h in the dark at 4°C. Chlorophyll a concentrations were measured with a 10-AU fluorometer (Turner Designs) (see Cooper et al. 2012).

At stations sampled by trawling from 7 May to 2 June 2006 and on 7 June 2007, duplicate 1 cm³ samples of surface sediments (1.54 cm² surface area) were collected from the top of a van Veen grab sample before opening the grab to minimize disturbance of the sediments. Ten milliliters of 90% acetone were mixed with each sample, which was stored at 4°C for 12 h to ensure extraction of all chlorophyll a. Chlorophyll a concentration within the acetone extract was then measured with the 10-AU fluorometer as described above. The mean of chlorophyll a measurements for the 2 samples at each station was scaled up to µg chlorophyll a per m² of surface sediments.

Se and organic N in sediments

Sediment samples were taken from the top of a van Veen grab as described above. These samples were analyzed for total Se with an oxidative digest followed by selective hydride generation/atomic absorption spectrometry (Cutter 1985). Total N concentration in sediments was measured with a Carlo Erba 1500 Elemental Analyzer by the procedures of Cutter & Radford-Knoery (1991).
**Table 1.** *Somateria fischeri.* Arithmetic means (µg g⁻¹ dry mass, ±SE), geometric means, and ranges of trace elements in liver, kidney, and pectoral muscle of 26 male and 12 female adult spectacled eiders in March 2001 in the north-central Bering Sea. *Significantly different from males, t-test, p < 0.05

<table>
<thead>
<tr>
<th></th>
<th>Arithmetic mean ± SE</th>
<th>Male Geometric mean</th>
<th>Range</th>
<th>Female Arithmetic mean ± SE</th>
<th>Geometric mean</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>Liver</td>
<td>235.59 ± 15.77</td>
<td>223.77</td>
<td>119.79–489.13</td>
<td>171.79 ± 12.23*</td>
<td>167.08</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>96.17 ± 4.75</td>
<td>93.93</td>
<td>70.54–174.28</td>
<td>97.37 ± 11.45</td>
<td>91.27</td>
</tr>
<tr>
<td></td>
<td>Muscle</td>
<td>24.40 ± 0.75</td>
<td>24.14</td>
<td>18.96–33.40</td>
<td>22.63 ± 1.25</td>
<td>22.26</td>
</tr>
<tr>
<td>Cd</td>
<td>Liver</td>
<td>36.20 ± 3.48</td>
<td>33.15</td>
<td>16.62–90.76</td>
<td>34.58 ± 5.65</td>
<td>30.75</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>163.42 ± 14.25</td>
<td>145.30</td>
<td>27.86–311.93</td>
<td>201.81 ± 22.99</td>
<td>181.83</td>
</tr>
<tr>
<td></td>
<td>Muscle</td>
<td>2.05 ± 0.32</td>
<td>1.63</td>
<td>0.54–8.30</td>
<td>2.66 ± 0.79</td>
<td>1.90</td>
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<tr>
<td>Hg</td>
<td>Liver</td>
<td>1.42 ± 0.06</td>
<td>1.39</td>
<td>0.75–2.09</td>
<td>1.18 ± 0.10*</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>0.72 ± 0.03</td>
<td>0.70</td>
<td>0.32–1.03</td>
<td>0.71 ± 0.06</td>
<td>0.69</td>
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<tr>
<td></td>
<td>Muscle</td>
<td>0.21 ± 0.01</td>
<td>0.20</td>
<td>0.13–0.32</td>
<td>0.17 ± 0.02</td>
<td>0.16</td>
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<tr>
<td>Cu</td>
<td>Liver</td>
<td>733.59 ± 81.05</td>
<td>607.43</td>
<td>34.50–2050.37</td>
<td>238.68 ± 47.35*</td>
<td>183.69</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>69.02 ± 4.48</td>
<td>65.74</td>
<td>31.69–131.17</td>
<td>76.83 ± 5.65</td>
<td>74.63</td>
</tr>
<tr>
<td></td>
<td>Muscle</td>
<td>16.14 ± 0.60</td>
<td>15.88</td>
<td>10.44–22.77</td>
<td>15.47 ± 0.87</td>
<td>15.21</td>
</tr>
<tr>
<td>Zn</td>
<td>Liver</td>
<td>129.99 ± 5.08</td>
<td>127.54</td>
<td>83.60–197.68</td>
<td>138.12 ± 10.86</td>
<td>133.46</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>131.28 ± 4.04</td>
<td>129.40</td>
<td>60.89–159.93</td>
<td>137.68 ± 5.34</td>
<td>136.41</td>
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<tr>
<td></td>
<td>Muscle</td>
<td>41.28 ± 1.29</td>
<td>40.85</td>
<td>32.79–61.54</td>
<td>43.49 ± 1.50</td>
<td>43.21</td>
</tr>
<tr>
<td>Pb</td>
<td>Liver</td>
<td>0.08 ± 0.01</td>
<td>0.07</td>
<td>0.03–0.29</td>
<td>0.05 ± 0.01*</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Kidney</td>
<td>0.29 ± 0.06</td>
<td>0.23</td>
<td>0.12–1.45</td>
<td>0.18 ± 0.02</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Muscle</td>
<td>0.06 ± 0.01</td>
<td>0.05</td>
<td>0.03–0.21</td>
<td>0.04 ± 0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Statistics**

We tested for differences between arithmetic means with t-tests, and with pairwise comparisons in ANOVAs. For trace element levels in spectacled eiders in their wintering area, geometric means based on log₁₀ are also reported. We used linear regressions to examine relationships between body condition and levels of different trace elements in liver and kidney, and among concentrations of different trace elements.

**RESULTS**

**Trace elements in spectacled eiders and other species**

In adult spectacled eiders south of St. Lawrence Island in late March 2001, concentrations of most common trace elements were not high enough to be considered toxic to birds (Table 1) (Eisler 2000). In contrast, concentrations of Se in liver and Cd in kidney were exceptionally high. Liver concentrations (arithmetic mean) in males exceeded those in females by 37% for Se (235.59 versus 171.79 µg g⁻¹ dry mass), 207% for Cu (733.59 versus 238.68 µg g⁻¹ dry mass), 20% for Hg (1.42 versus 1.18 µg g⁻¹ dry mass), and 60% for Pb (0.08 versus 0.05; t-tests, p < 0.05). In kidneys, there were no significant differences between sexes in levels of any trace element measured.

**Effects on body condition**

There was no relationship in either adult males or adult females between liver Se and total body lipid or size-adjusted total body protein (all r² < 0.10, p > 0.22). The same was true for liver Hg (all r² < 0.17, p > 0.18), liver Cu (all r² < 0.16, p > 0.15), and kidney Cd (all r² < 0.08, p > 0.19). Thus, variations in these trace elements did not appear to affect the fat or protein reserves of adult spectacled eiders on their main wintering area.

**Relationships among elements**

In the livers of males or females, there was no relationship between levels of Se and Hg (r² < 0.04, p > 0.41), or between Se and Cu (r² < 0.09, p > 0.16). Liver Se was related to kidney Cd in males (r² = 0.26, p = 0.01) but less clearly so in females (r² = 0.26, p = 0.09). Liver Cu was positively related to liver Hg (r² = 0.33, p = 0.05) and kidney Cd (r² = 0.48, p = 0.01) in females, while there were no correlations in males (both r² < 0.06, p > 0.25).
Spatiotemporal changes in Se burdens

Spectacled eiders begin leaving their main wintering area in March and most have left by late April (Lovvorn et al. 2003, Larned et al. 2012). Males collected in May near the village of Gambell along the northwest coast of St. Lawrence Island (Fig. 2), where spectacled eiders normally do not occur in appreciable numbers during winter, had much lower mean values of liver Se than males collected 2 mo earlier on the main wintering area (Fig. 3). The males collected off Gambell in May appear to have been belated migrants, or perhaps were from the small breeding population on St. Lawrence Island. It is unlikely that lower Se concentrations in the Gambell eiders (Table 1, Fig. 3) resulted from any increase in liver mass while total content of Se remained unchanged: in 25 adult male spectacled eiders collected south of St. Lawrence Island, there was no correlation between liver fresh mass and liver Se concentration over a range of liver fresh mass from 46 to 86 g (r² < 0.01, p = 0.72).

We compared liver concentrations of Se measured in and near the wintering area with liver concentrations estimated from blood samples taken in breeding areas. Correlations between Se levels in liver versus blood can be variable (Wayland et al. 2001a), so predicted concentrations in liver should be interpreted only as indicating qualitative trends. Nevertheless, the validity of these estimates is supported by data from the North Slope, where the mean (±SE) liver Se concentration (144 ± 8 µg g⁻¹ dry mass) predicted from blood samples in 14 adult males during 5 to 16 June 1996 (Wilson et al. 2004) did not differ from direct measures of liver Se in 4 adult males that died of various causes from 27 May to 21 June 2003 to 2006 (163 ± 29 µg g⁻¹ dry mass; t-test, p = 0.53; M. W. Miller, C. J. Latty, and A. C. Matz, US Fish and Wildlife Service, unpubl. data). Although liver Se concentrations (µg g⁻¹ dry mass) in spectacled eiders may vary some from year to year, the difference between late winter (measured values) and soon after arrival on breeding areas (estimated values) averaged 44 in males and 66 in females for the Y-K Delta, and 92 in males and 109 in females for the North Slope. We expect that these large differences well exceed annual variations at the same locations.

Based on liver Se concentrations estimated from blood samples, Se burdens in both males and females declined from the time the eiders left the main wintering area south of St. Lawrence Island until shortly after they arrived on breeding areas on the Y-K Delta and North Slope (cf. Fig. 1, Fig. 3). Reasonable estimates of periods between departure from the wintering area and arrival at inland breeding sites (Fig. 1) are about 4 wk for the Y-K Delta and 8 wk for the North Slope and probably Siberia (Lovvorn et al. 2003). Appreciable depuration of Se could occur during those periods if exposure was reduced (Heinz et al. 1990). Apparent declines in liver Se during these migration periods (Fig. 3) suggest that foods consumed by eiders en route from wintering to breeding areas had much lower Se levels than foods on the wintering area itself. As noted previously at both nesting sites (Grand et al. 2002, Wilson et al. 2004), Se in adult females decreased throughout the breeding period to relatively low levels, and ducklings raised in those areas did not accrue appreciable Se (Fig. 3).
Comparisons with other sea duck species

Compared with levels in other sea duck species that had fed mainly in marine habitats, concentrations of Se and Cd in spectacled eiders during late winter were exceptionally high (Table 2). To our knowledge, liver Se levels in spectacled eiders in the present study (up to 489 µg g\(^{-1}\) dry mass) are the highest ever reported in free-living birds (Eisler 2000). Maximum kidney Cd (312 µg g\(^{-1}\) dry mass) of

Table 2. Geometric means (µg g\(^{-1}\) dry mass) and ranges of Se, Hg, Cu, and Zn in livers, and of Cd in kidneys, of mostly adult, carnivorous diving ducks during the nonbreeding period in various marine locations. Also included are common eiders, king eiders, and long-tailed ducks from the breeding period (br), when common eiders feed in marine habitats, and king eiders and long-tailed ducks in freshwater habitats. B = both sexes

<table>
<thead>
<tr>
<th>Species</th>
<th>Location</th>
<th>Sex</th>
<th>Se</th>
<th>Hg</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
<th>Source</th>
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</thead>
<tbody>
<tr>
<td>Spectacled eider</td>
<td>North-central Bering Sea, USA</td>
<td>M</td>
<td>224</td>
<td>1.4</td>
<td>145</td>
<td>607</td>
<td>128</td>
<td>1</td>
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<td></td>
<td></td>
<td>F</td>
<td>167</td>
<td>1.1</td>
<td>182</td>
<td>184</td>
<td>133</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Near Gambell, Bering Sea, USA</td>
<td>M</td>
<td>124</td>
<td>1.1</td>
<td>96</td>
<td>559</td>
<td>158</td>
<td>2</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(108–264)</td>
<td>(0.6–2.2)</td>
<td>(48–305)</td>
<td>(37–528)</td>
<td>(76–223)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(78–171)</td>
<td>(0.8–1.7)</td>
<td>(50–137)</td>
<td>(123–1333)</td>
<td>(136–210)</td>
<td></td>
</tr>
<tr>
<td>Common eider</td>
<td>Spitsbergen, Norway</td>
<td>B</td>
<td>30</td>
<td>3.3</td>
<td>61</td>
<td>900</td>
<td>167</td>
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<td>(37–113)</td>
<td>(23–3833)</td>
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aArithmetic mean; bMedian; c95% CI
wintering spectacled eiders was also 34% higher than the highest previously reported for sea ducks; geometric means of 145 µg g\(^{-1}\) dry mass for males and 182 for females were rivaled only by values for king eiders *Somateria spectabilis* in the eastern Canadian Arctic. Except in areas subject to high anthropogenic loading, such as San Francisco Bay, Hg was not elevated in sea ducks that were using marine habitats (Table 2).

### Hydrographic advection of bloom materials

Our cruise in May to early June 2007 occurred during and after the ice-edge bloom and documented the sinking of that material to the sea floor (Cooper et al. 2012). As the ice pack breaks up and is moved around by wind, phytoplankton blooms develop irregularly in the shifting mosaic of ice and open water. Locations where intense phytoplankton blooms occurred in the water column, as indicated by chlorophyll concentrations integrated across all depths, differed from locations where most chlorophyll accumulated in the sediments (Fig. 4). Rather, bloom material produced throughout the area appeared to be advected, presumably by bedload transport after it settled, into a region of high chlorophyll concentration in sediments in the west-central part of the study area. Multibeam sonar measurements show no major bathymetric depression in that area, suggesting that bloom materials were transported into a persistent eddy at that location. A gyre there was also predicted by a model of wind-driven hydrography (Overland & Roach 1987). This ‘steady eddy’, as inferred from consistent organic accumulation and high biomass of benthic deposit feeders, persisted in this general area southwest of St. Lawrence Island from at least as early as 1990 through 2007 (Cooper et al. 2002, 2012). These data suggest that inputs of trace elements by currents or atmospheric deposition do not have to occur directly above benthic feeding areas to become locally concentrated there. Rather, assimilation or adsorption of elements by bloom materials, and sinking of those materials to the bottom, can occur over a larger expanse with subsequent hydrographic concentration into a limited region (Yao & Zhang 2005).

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**Fig. 4.** Chlorophyll a concentrations (mg m\(^{-2}\)) in surface sediments (isopleths) and integrated over the water column (color gradients) from 18 to 29 May 2007 south of St. Lawrence Island in the Bering Sea. Red arrow indicates station CD1, where spectacled eiders were collected for this study on 19 to 22 March 2001.
Trace elements in bivalve prey and sediments

Esophagi of spectacled eiders collected near station CD1 in the study area in March 2001 (Fig. 4) contained almost exclusively the bivalve *Nuculana radiata* (Lovvorn et al. 2003). In May and early June 2007, concentrations of Se and Cd in soft tissues of *N. radiata* from the steady eddy region were substantially higher than in specimens from the surrounding area (Fig. 5). To portray the magnitude of this spatial effect, at 7 adjacent stations that represent the core of this region of high values, mean (±SD) tissue concentrations were 33% higher for both Se (2.36 ± 0.37 versus 1.78 ± 0.23 µg g⁻¹ dry mass) and Cd (6.38 ± 0.90 versus 4.79 ± 1.06 µg g⁻¹ dry mass) than at the 13 other stations (t-tests, p < 0.01).

Moreover, at 3 stations within the core of the steady eddy region, and at 3 stations in peripheral areas outside that region (as determined by much lower sediment organic content), *Nuculana radiata* was sampled just as bloom materials were starting to settle on the bottom and again 2 to 3 wk later when settled bloom materials had been redistributed into the eddy. Within the eddy core, concentrations in *N. radiata* increased by 53% in Se (t-test, p = 0.007) and 34% in Cd (p = 0.087) over that period. However, outside that core region, levels in *N. radiata* decreased by 8% in Se (p = 0.099) and by 16% in Cd (p = 0.036). These changes suggest that redistribution of settled bloom materials into the steady eddy was accompanied by short-term changes in trace element availability to these bivalves. Although these short-term changes illustrate transport processes by which element concentration might occur in May to early June, spectacled eiders do not feed in this area until 9 to 12 mo later (January to April). By that time, we expect that high rates of bioturbation will have thoroughly mixed the fresh detritus and associated elements into the large and long-term pool of sediment organic matter that provides food for deposit feeders for most of the year (Lovvorn et al. 2005). Although this mixing would not alter overall spatial patterns of deposition among sites, it probably dampens between-year variations within sites.

Total Se levels in surface sediments also reflected concentration of materials within the steady eddy (Fig. 6; sediments were analyzed for Se at fewer stations than were bivalves). At 6 of the stations within the eddy core mentioned above, the mean (±SD) total Se level in sediments (0.49 ± 0.13 µg g⁻¹ dry mass, range 0.29–0.61) was 34% higher (t-test, p = 0.01) than at 9 stations outside that area (0.37 ± 0.07, range 0.28–0.47). Concentrations of Se in soft tissues of *Nuculana radiata* increased with increasing total Se in sediments (r² = 0.40, p < 0.01, n = 16 stations),

![Fig. 5. Tissue concentrations (ppm; µg g⁻¹ dry mass) of (A) Se and (B) Cd in the bivalve *Nuculana radiata* at stations south of St. Lawrence Island in the Bering Sea. Among the 7 adjacent stations with high element levels in the northwest corner of the sampling grid, one station is obscured](image)

![Fig. 6. Total Se concentrations (µg g⁻¹ dry mass) in surface sediments at stations south of St. Lawrence Island in the Bering Sea](image)
especially at sediment Se levels ≥0.3 µg g⁻¹ (r² = 0.81, p < 0.01, n = 13). Moreover, atomic (molar) ratios of C:N (mean ± SD) in surface sediments (9.08 ± 0.70, range 8.20–10.24, n = 16) were within the range for pure cultures of 11 phytoplankton species (Doblin et al. 2006), suggesting a high fraction of settled phytoplankton.

We compared concentrations of Se and Cd in *Nuculana radiata* from the steady eddy region with values reported for bivalves and sediments at other north-temperate and Arctic sites. Concentrations of Se in *N. radiata* from the 7 stations at the core of the steady eddy (1.86 to 2.84 µg g⁻¹ dry mass; Fig. 5) were in the range of values reported for other bivalve species from industrialized areas with known Se contamination, such as San Francisco Bay (USA), the Wadden Sea (Netherlands), the White Sea (Russia), and contemporary coastal China (Table S1 in the Supplement). Exceptions to this similarity in concentrations were *Mytilus edulis* in Trondheimsfjorden, Norway, and *Potamocorbula amurensis* in San Francisco Bay, both filter feeders (versus deposit feeders) with much higher Se levels. Concentrations of Cd in *N. radiata* from the steady eddy core (5.32 to 7.82 µg g⁻¹ dry mass) were higher than all other values reported for bivalves, including heavily industrialized sites. Thus, mechanisms that concentrated Se and Cd in the steady eddy can result in levels in bivalves that rival those in areas with known contamination (e.g. Ohlendorf et al. 1986). In sediments, mean (±SE) concentrations of Se within the steady eddy (0.49 ± 0.13 µg g⁻¹ dry mass) were within ranges reported for a variety of estuarine and nearshore areas in the Pacific and North Atlantic Oceans (Table S2 in the Supplement).

**DISCUSSION**

**Tolerance and accumulation of high trace element levels**

For spectacled eiders in March 2009, there was no evidence that their very high burdens of Se or Cd affected their total body fat or protein. Although tissue concentrations of Se and Cd in our study were up to an order of magnitude higher, our results are consistent with findings for other diving ducks in which correlations of these elements with body fat and protein were low or even positive (Takekawa et al. 2002, Anteau et al. 2007). Our results also concur with assays for spectacled eiders near Gambell in May 1995 (Fig. 2, Table 2), which showed no effects of elevated trace elements on histopathology or a range of biochemical biomarkers (Trust et al. 2000). Despite moderately high levels of Se, Cd, and Hg in common eiders of the Canadian Arctic, there were no effects on immune response, corticosterone levels, or liver glycogen concentrations (Wayland et al. 2003). For captive common eiders fed high Se in food (20 µg g⁻¹ fresh mass), resulting liver concentrations (mean ± SE = 351 ± 25.1 µg g⁻¹ dry mass, range 234–408 µg g⁻¹ dry mass) were in the range of those in spectacled eiders in our study (Franson et al. 2007) (Table 1). In these captive common eiders, there were no effects on body mass or on most of a number of biochemical indices of health. However, there were lesions in liver and in feather pulp in about half of the experimental eiders, and some oxidative stress as evidenced by glutathione indicators.

As to impacts on reproduction, high Se in the blood of spectacled eiders on the Y-K Delta had no detectable effects on nest success or egg viability (Grand et al. 2002). Similarly, moderately high liver Se in wild white-winged scoters *Melanitta fusca* (mean 33 mg g⁻¹ dry mass, range 4–75 mg g⁻¹ dry mass) had no apparent effects on female body condition or breeding propensity (DeVink et al. 2008). In interior Alaska, liver Se of adult white-winged scoters averaged 54 µg g⁻¹ dry mass; however, eggs taken from oviducts contained <4.7 µg g⁻¹ dry mass, suggesting that transfer of Se from the mother’s liver to eggs can be far less than inferred for freshwater ducks and other waterbirds (Henny et al. 1995). In contrast to these large sea ducks, liver Se above 20 µg g⁻¹ dry mass has an array of toxic effects on behavior, reproduction, and long-term survival of mallards and other freshwater birds (Heinz 1996). Taken together, these data indicate that marine ducks can tolerate exceptionally high levels of some trace elements and especially Se, with minimal effects on adult health or reproduction.

Accumulation of Se may be beneficial if Se acts to detoxify Hg (Heinz & Hoffman 1998). It appears that Se detoxifies inorganic Hg (derived from methylmercury ingestion) by forming HgSe (Ikemoto et al. 2004). However, in a number of marine birds, Se levels are often well in excess of a 1:1 molar ratio with Hg, and the magnitude (and sometimes direction) of correlation is highly variable (Norheim 1987, Goede & Wolterbeek 1994, Trust et al. 2000, Wayland et al. 2001b, Ikemoto et al. 2004). In the livers of wintering male spectacled eiders, the ratio of Se:Hg (arithmetic means) was 166:1 (Table 1). In their main bivalve prey (*Nuculana radiata*), Hg concentrations...
were below detection limits in 13 of 18 station samples, and at the other 5 stations averaged only 0.55 µg g⁻¹ dry mass (range 0.14 to 1.32 µg g⁻¹ dry mass). Assessment of Hg−Se interactions may be aided by discriminating inorganic from organic forms of both elements in tissues (Scheuhammer et al. 1998), which was not done in our study. Nevertheless, in wintering spectacled eiders, the very high levels of Se and quite low levels of Hg in tissues and foods indicate that the high Se was not accumulated to detoxify Hg.

Other potential physiological interactions among trace elements are multiple and complex (Eisler 2000). These interactions include protective effects of Se against Cd, a mechanism perhaps suggested by our finding of a positive correlation (r² = 0.26) between Se and Cd in spectacled eiders. Positive correlations among concentrations of different elements (e.g. Norheim 1987) do not necessarily indicate physiological interactions, but perhaps only simultaneous exposure. The extent to which Se in livers of wintering spectacled eiders is being accumulated to protect against Cd is unclear, but as for Hg this effect seems unlikely to explain the very high levels of Se observed.

The high concentrations in wintering spectacled eiders likely resulted not only from inherently high physiological accumulation, but also from high and sustained exposure in food. When captive common eiders were fed Se at 20 µg g⁻¹ fresh mass of food, their mean (±SE) liver concentration of Se was 351 ± 25.1 µg g⁻¹ dry mass (Franson et al. 2007). When mallards were fed similar Se concentrations in food (20, 25, and 29 µg g⁻¹ fresh mass), their mean liver Se concentrations were only 49, 30, and 32 µg g⁻¹ dry mass, respectively (see Franson et al. 2007). Spectacled eiders in our study accumulated liver Se up to 489 µg g⁻¹ dry mass (mean 215 µg g⁻¹) when eating bivalves that contained only 8 µg g⁻¹ fresh mass Se in soft tissues (2.4 µg g⁻¹ dry mass; Table S1 in the Supplement). Thus, both experimental and field data show that if eiders and some other sea ducks are exposed to Se, they can accumulate high levels to which they are quite tolerant physiologically.

How could spectacled eiders during winter have achieved such high liver Se concentrations while feeding on clams containing relatively low levels of Se? It is standard practice in experimental studies to report exposure in terms of concentrations in food. However, exposure depends not only on concentrations in food, but also on the total amount of food eaten. Flightless eiders living at temperate latitudes in pens where they feed on pelleted food from pans have much lower food requirements than free-rang-
sea (Grand et al. 2002). Similar patterns have been reported in other bird taxa. Among dunlins *Calidris alpina* in western Europe, Se concentrations in kidneys were ~26 µg g⁻¹ dry mass for birds in the marine environment, but declined rapidly to ~7 µg g⁻¹ dry mass when they moved to freshwater breeding sites (Goede et al. 1989). Emperor geese *Chen canagica*, which winter in marine habitats of the Aleutian Islands, showed similar declines in Se when they moved into nesting areas in the Y-K Delta (Franson et al. 1999).

In spectacled eiders, substantial declines in levels of Se and Cd from the wintering area in March to spring migration in May (Table 2), and apparent further decline in Se before arrival at nesting sites on the Y-K Delta and North Slope (Fig. 3), indicate especially high exposure to these elements in the wintering area. These patterns suggest that other marine habitats used by the eiders during 4 to 8 wk of spring migration have lower availability of Se than their main wintering site.

**Reasons for high Se and Cd in the eider wintering area**

In marine birds, levels of trace elements often vary widely in benthivores among locations, and between benthivores and water-column feeders in the same area (Norheim 1987, Dietz et al. 1996, Kim et al. 1996a, Savinov et al. 2003, Mallory et al. 2004). Although such data are routinely gathered, there has been little attempt to explain those variations in terms of atmospheric or oceanographic processes. Our study indicates that the spectacled eider wintering area in the north-central Bering Sea is a site of exceptional exposure to Se and Cd. What factors might contribute to that situation?

**Hydrographic and atmospheric supply of trace elements**

Upwelling and hydrographic transport may supply trace elements to the eider wintering area. It is likely that Se and Cd upwelled along the Bering Shelf break (Kremling 1983, Cutter & Bruland 1984) are transported northward along the western edge of the shelf in the Anadyr Current (Fig. 2). A minor branch of the Anadyr Current diverges eastward south of St. Lawrence Island, perhaps injecting trace elements into that region (Fig. 2). This effect may be enhanced by the fact that in North Pacific waters that flow northward into the Bering Sea, dissolved and particulate Cd concentrations are 3 to 5 times higher than in the North Atlantic (Bruland et al. 1994), and dissolved Se concentrations are 2 to 3 times higher than at lower latitudes in the North Pacific (Cutter & Bruland 1984, Ranville et al. 2010).

Beyond such hydrographic inputs, supply of soluble Se and Cd to the oceans, especially in Arctic regions, often includes substantial contributions by atmospheric transport from distant sources (Cutter & Cutter 1998, Ranville et al. 2010). Even on shallow shelves where trace element availability in surface waters is often higher than in the deep ocean, atmospheric inputs can dominate the supply of elements to meet high demands of blooming phytoplankton (Guieu et al. 2010). In the South China Sea, often 98% or more of trace elements in sinking particles was derived from aeolian deposition of highly soluble anthropogenic aerosols (Ho et al. 2010).

An atmospheric supply of anthropogenic trace elements, associated with particles from dust storms at inland deserts, flows from central Asia northward through the Bering Sea region, where there is substantial deposition of aerosols (Arimoto et al. 2006). Indeed, Ranville et al. (2010) documented elevated Se in surface waters of the North Pacific just south of the Bering Sea that were paralleled by enhanced aerosol Se concentrations in the same region. Based on air mass trajectories, elemental ratios, and enrichment factors, they attributed the elevated atmospheric and water-column Se concentrations to Asian fossil fuel emissions. Atmospheric transport of Asian trace elements is greatest in March to May (Yu et al. 2008), so deposited aerosols may create a pulse of availability for the major spring bloom that occurs in the receding marginal ice zone during this period. Deposited Cd that accumulates on sea ice and is released when the ice melts can increase Cd concentrations in surface waters by 2 to 3 times over pre-melt values (AMAP 1998).

**Element concentration and settling in blooming phytoplankton**

Aside from environmental inputs, biological mechanisms also mediate the supply of trace elements to the benthos. Because demand for trace elements by blooming phytoplankton is so high, available trace elements are rapidly taken up, with algal cells sequestering elements even to surplus levels if availability allows (Fisher et al. 1984, Baines & Fisher 2001). Se is an essential micronutrient for phyt-
plankton, and Cd is a metalloenzyme component in diatoms (Lane et al. 2005). Moreover, conditions of low Zn typical of marine waters can cause phytoplankton to substitute Cd for Zn (Lane & Morel 2000), and accumulation of Cd by phytoplankton can also increase under Fe limitation (Lane et al. 2008). Bacteria colonizing senescing bloom phytoplankton can similarly concentrate these elements, either within the bacterial cells or in exopolymer secretions (Dixon et al. 2006, Ueshima et al. 2008). If bloom particles sink about 100 m d−1 (Fisher & Reinfelder 1995), in the shallow waters south of St. Lawrence Island (mostly 40 to 80 m), inputs of Se and Cd from currents or the atmosphere may be taken up or adsorbed and transported to the bottom within days (cf. Noriki et al. 1985).

Both Se and Cd exhibit ‘nutrient-type’ behavior in the water column. Such elements are often acutely depleted in near-surface waters via assimilation by phytoplankton or adsorption to biogenic materials, which then sink to greater depths, where the elements are released through mineralization (Bruland et al. 1994). Of all trace metals, Cd exhibits the most extreme nutrient-type behavior (Bruland 1992). Without resupply by upwelling, currents, or atmospheric deposition, such elements can be stripped from near-surface waters by high rates of biogenic uptake (Jones & Murray 1984, Bruland 1992). Nevertheless, despite very low concentrations, it appears that in most cases neither Se nor Cd is limiting to phytoplankton growth relative to P or N (Jones & Murray 1984, Cid et al. 2011).

However, neither Se nor Cd must be limiting to phytoplankton production for additional inputs of these elements to be removed from the water and concentrated in settling bloom materials. Much of Cd and some Se can reach the bottom by extracellular adsorption or ligand binding to such particles (Bruland 1992, Cohen et al. 1992, Fisher & Reinfelder 1995). In the South China Sea, most Cd in sinking particles was incorporated intracellularly into biogenic organic matter (Ho et al. 2010). However, for other trace elements (including Cu and Zn; Se was not studied), the intracellular fraction was an insignificant portion of those elements in sinking particles, with most elements being adsorbed to the surface of biogenic particles. On the Bering Sea shelf in early September (3 to 4 mo after the spring bloom), supply of Cd (Se was not studied) was not limiting to phytoplankton production relative to N or P (Cid et al. 2011). However, even long after the spring bloom, assimilation or adsorption by sinking particles resulted in depletion of Cd in surface waters. These results suggest that during the brief but intense ice-edge spring bloom, additional inputs of Se and Cd from currents or the atmosphere could result in accumulation of these elements in settled organic matter (cf. Yuan & Zhang 2006).

Boundary-layer transport and concentration in benthic food webs

Studies reviewed above clearly established that inputs of nutrient-type trace elements from currents or the atmosphere are often quickly transported to sediments by settling bloom material. However, the exceptional levels of Se and Cd in spectacled eiders in their main wintering area, and localized concentrations in sediments and bivalves (Figs. 5 & 6), suggest further concentrating mechanisms. Exposure of eiders to Se appeared to decline once they left their wintering location and traveled through other marine areas (Fig. 3).

Following the main spring bloom in late May 2007, chlorophyll in sediments indicated a major pulse of settling phytoplankton south of St. Lawrence Island (Cooper et al. 2012). However, chlorophyll measurements showed that the dispersion of intense blooms in the water column did not correspond to the dispersion of chlorophyll in sediments (Fig. 4). Instead, most sediment chlorophyll in our 190 × 270 km study area had been concentrated in less than a quarter of that region, which corresponded to the main use area of spectacled eiders (Fig. 2). Sediments in this zone have much higher organic content and oxygen demand than elsewhere in the study area, as well as much higher biomass of benthic invertebrates (Cooper et al. 2002, 2012).

As there is no evident bathymetric depression in this area, it appears that this region is characterized by a persistent eddy into which chlorophyll deposited over a much larger region is transported by bedload or boundary-layer advection. A gyre in this location was in fact predicted by wind-driven hydrographic models (Overland & Roach 1987). Local tidal currents are relatively weak (Danielson & Kowalik 2005), so the distribution of sediment grain sizes and particulate organic matter largely reflects local wind patterns over this shallow region of the shelf (40 to 90 m). As a result, the exact location of eddy accumulation can shift among years (Cooper et al. 2002). Such variations in local inputs of contaminants are dampened by the life spans of benthic organisms (most bivalves eaten by spectacled eiders in 2001 were probably 6 to 9 yr old), and by the large, per-
sistent pool of sediment organic matter that likely buffers the stock of trace elements in sediments (see Lovvorn et al. 2005). In the eider wintering area, this transport mechanism may lead to local accumulation of Se and Cd that settled from the water column over a much larger region. Such effects would be less prominent in areas such as the main migration sites of spectacled eiders along the Chukchi Sea coast (Fig. 1), where prevailing currents or wave action tend to inhibit long-term accumulation of sediment organic matter in large, persistent patches (J. R. Lovvorn, S. C. Jewitt, and D. Dasher, unpubl. data). When passing through that coastal area on the way to breeding sites on the North Slope, Se levels in eiders appeared to decline (Fig. 3).

Within the conspicuous region of high organic accumulation in the wintering area (Fig. 4), deposit-feeding bivalves that are the main prey of spectacled eiders, were exceptionally abundant in 2001 when the eiders for this study were collected there (Lovvorn et al. 2003, 2009). Deposit feeders readily take up Se and Cd from ingested algae, settled organic matter, and associated bacteria (Schlekat et al. 2002, Ueshima et al. 2008, Sokolowski et al. 2005). Levels of Se and Cd in sediments and bivalves from the persistent eddy region were higher than in the surrounding area (Figs. 5 & 6), suggesting that local accumulation of element-bearing organic matter increased uptake by the deposit-feeding prey of eiders (Thorsson et al. 2008). Moreover, Se and Cd concentrations in bivalves in the core of the steady eddy increased by 53% (Se) and 34% (Cd) from the time of our first sampling to 2 to 3 wk later, although intense blooms in the water column had occurred elsewhere (Fig. 4). Outside the eddy core, element concentrations in Nuculana radiata decreased by 8% in Se and 16% in Cd.

Physiological, atmospheric, and oceanographic effects on element levels

Our results and those of others show that high trace element levels in eiders and some other sea ducks reflect an inherent physiological tendency to accumulate these elements. However, wide variations in tissue concentrations indicate that relative exposure differs greatly among regions, and among localities within the same region. Our data and information reviewed here suggest that oceanographic concentration of settling organic matter, enriched by trace element inputs from currents or atmospheric deposition, can be an important determinant of geographic variations in contaminant exposure of bottom-feeding marine birds.

The coupling of high physiological uptake in some marine organisms with oceanographic mechanisms that concentrate trace elements may increase in importance as production of pollutants increases worldwide. For example, in the Pacific region, China has more than doubled its atmospheric emissions in the last 2 decades, and the current explosive growth of industrial and domestic pollutants is expected to continue (Yu et al. 2008). Although effects of these inputs on climate, incident solar radiation, crop yields, and human health have been examined (see Yu et al. 2008), effects on ocean food webs have not. In this region, as elsewhere, we urge that studies of trace element levels in marine predators be combined with atmospheric and oceanographic investigations to help explain observed geographic patterns and predict future trends.

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